



Short communication

Reduction of iodine complexed with sulfoxides and organophosphorus esters near 4.0 V vs. Li/Li⁺

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HIGHLIGHTS

- We detected reduction of iodine in organic solvents over +1.0 V vs. NHE.
- The organic solvents were sulfoxides and trimethyl phosphate.
- Li–iodine batteries using those iodine solutions drive voltages near +4.0 V.

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ABSTRACT

It is accepted that the reduction of iodine species in non-aqueous solvents occurs through one-electron or two-electron processes below roughly 3.5 V vs. Li/Li⁺. In some iodine solutions, the molecular complexation of iodine with the organic solvent proceeded via a charge–transfer interaction. Reduction of iodine in non-aqueous solvents having S=O or P=O groups, as well as interactions of iodine molecules with these solvents, were studied. Iodine molecules associated with dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), and trimethyl phosphate (TMP) showed anomalous reduction above +1.0 V vs. NHE. We demonstrated the operation of lithium–iodine batteries using DMSO, TMSO and TMP near 4.0 V vs. Li/Li⁺.

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1. Introduction

A significant improvement in the field of batteries is required to meet the demands of future vehicles, electronics and many other applications. Gas-utilizing batteries using O₂ [1–3] or a mixture of O₂ and CO₂ [4] have attracted much attention as major candidates for future alternative energy sources. In these batteries, the solubility of the gasses strongly affects cell performance. Halogens such as iodine, bromine, and iodine chloride also dissolve in organic solvents at high concentrations. Like gas-utilizing batteries, Li–halogen batteries have sparked great interest and have been studied with the goal of developing next-generation batteries.

The redox potentials (E_0) of iodine species have already been investigated. The value of E_0 for the I₂/I₂^{•−} redox couple is known to be +0.11 V vs. NHE, with more recent estimates placing it at +0.21 V

[5]. For the two-electron reduction of iodine, the value of E_0 is +0.53 V. The reduction of I₃[−]/3I[−] has been measured to be +0.33 V. As the discharge voltage of the lithium–iodine (Li–I₂) battery is determined by the electrode potentials for the oxidation of Li and the reduction of iodine species, the Li–I₂ batteries in non-aqueous electrolytes drive voltages below 3.5 V [6–8]. Theoretically, these batteries cannot operate at 4.0 V.

It is well known that iodine molecules form molecular complexes with organic solvents such as sulfoxides, organophosphorus esters, phosphine sulfide, alkylamines, and propionitrile [9–12]. The formation of a 1:1 molecular complex between I₂ and a solvent molecule is caused by a charge–transfer interaction between functional groups (e.g., C=O, S=O, P=O) in the solvent (as the donor) and the σ bond of the iodine molecule (as the acceptor) [13]. The energy of complex formation, $-\Delta H$, for some organic solvents has been discussed by Drago et al. [14], and lies between 1.5 kcal mol^{−1} and 7.8 kcal mol^{−1}. For tri-*n*-butyl phosphate, $-\Delta H$ was found to be 2.94 kcal mol^{−1} by Tsubomura and Kliegman [11]. It was maintained that the reduction of iodine is

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influenced by the energy of complex formation. Cyclic voltammetry of iodine solutions in which iodine was associated with various electrolyte solvents was carried out. Here, we report that the molecular complexes between iodine and sulfoxides or organophosphorus esters have high were enhanced after reduction potentials, near +1.0 V vs. NHE. We have demonstrated that Li–I₂ batteries using these solvents show voltages near 4.0 V.

2. Experimental

2.1. Cyclic voltammograms (CV)

Cyclic voltammograms (CV) of iodine solutions were measured for the oxidation and reduction of iodine using a potentiostat–galvanostat (IVIUM Technologies, XR) at a scan rate of 10 mV s^{−1} with a Pt counter electrode and a carbon working electrode. Pt mesh (Nilaco Corporation) and lithium foil (Honjo Metal Co. Ltd.) were used as a reference electrode. The carbon electrode was prepared by dry-mixing Ketjen black (85%, Mitsubishi Chemical, ECP-600JD) with Teflon powder as a binder (15%, Daikin, T-104). The carbon electrode (weight 5 mg, area 1.0 cm², thickness 0.13 mm) was compressed on a Pt mesh and used as a cathode. The CV measurement was carried out in a 50 mL beaker cell containing the iodine solution composed of iodine (15 mg, Aldrich, 99.99%) and an organic solvent (12 mL) containing 0.1 mol L^{−1} tetrabutylammonium hexafluorophosphate (Aldrich) as a supporting salt. The organic solvents used were dimethyl sulfoxide (DMSO, NMR grade, Wako Chemical), tetramethylene sulfoxide (TMSO, Aldrich), trimethyl phosphate (TMP, Tokyo Kasei), or propylene carbonate (PC, Tomiyama Pure Chemical Industries Ltd.). When the reference electrode was lithium foil, LiPF₆ (Tomiyama) was used as a supporting salt.

2.2. UV–visible absorption spectra

UV–visible (UV–vis) absorption spectra of iodine solutions were recorded on a UV–vis spectrophotometer (Shimadzu, UV-2100) in the range of 200 nm–600 nm.

2.3. Measurement of the discharging behavior

Electrochemical cells were fabricated with a carbon cathode, Li anode, and an electrolyte solution containing iodine in a beaker cell under argon. A carbon sheet (weight 5 mg, area 1 cm², thickness 0.16 mm) prepared by dry mixing of Ketjen black (85%) and Teflon powder as a binder (15%) was compressed on a Pt mesh as the cathode. The separation between the cathode and the anode was 2 cm. The electrolyte was 1 mol L^{−1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, a supporting salt) solution in various solvents. LiTFSI was purchased from Kanto Chemical. The amounts of the electrolyte solution and iodine were 12 mL and 230 mg, respectively. The concentration of iodine in the solutions was 0.075 mol L^{−1}.

The discharging behavior of the electrochemical cells was measured with a Hokuto Denko potentiometer (HJ1001SM8A) using a 0.05 mA discharge current at room temperature.

2.4. Analysis of discharge reaction

Raman spectroscopy was carried out by a JASCO laser Raman spectrophotometer (NRS 3300) to study the discharge reaction. The wavelength of excitation was 532 nm.

Time of flight-secondary ion mass spectrometry (TOF-SIMS) measurements on the cathodes before and after discharging were

performed using a TOF-SIMS spectrometer (ION-TOF GmbH, TOFSIMS-5). The area of the SIMS analysis was 0.5 mm × 0.5 mm.

Gas chromatography mass spectrometry (GC/MS) was made by using a GC/MS spectrometer (Agilent Technologies, GSG9810) to investigate gas composition in the electrochemical cells after discharging. The constant flow rate of argon was 7 ml min^{−1}.

3. Results and discussion

3.1. CV profiles

Typical CV profiles of dilute iodine solutions are displayed in Fig. 1a and b. Fig. 1a shows CV profiles using a Pt reference electrode. In the iodine-PC solution (profile D in Fig. 1a), two reduction peaks appeared at +0.48 V and +0.02 V, reflecting the I₂/2I[−] and triiodide I₃[−]/3I[−] potentials, respectively. Meanwhile, three reduction peaks were detected in the iodine-TMSO solution (profile B): an I₂/2I[−] reduction peak at +0.32 V and an I₃[−]/3I[−] reduction signal

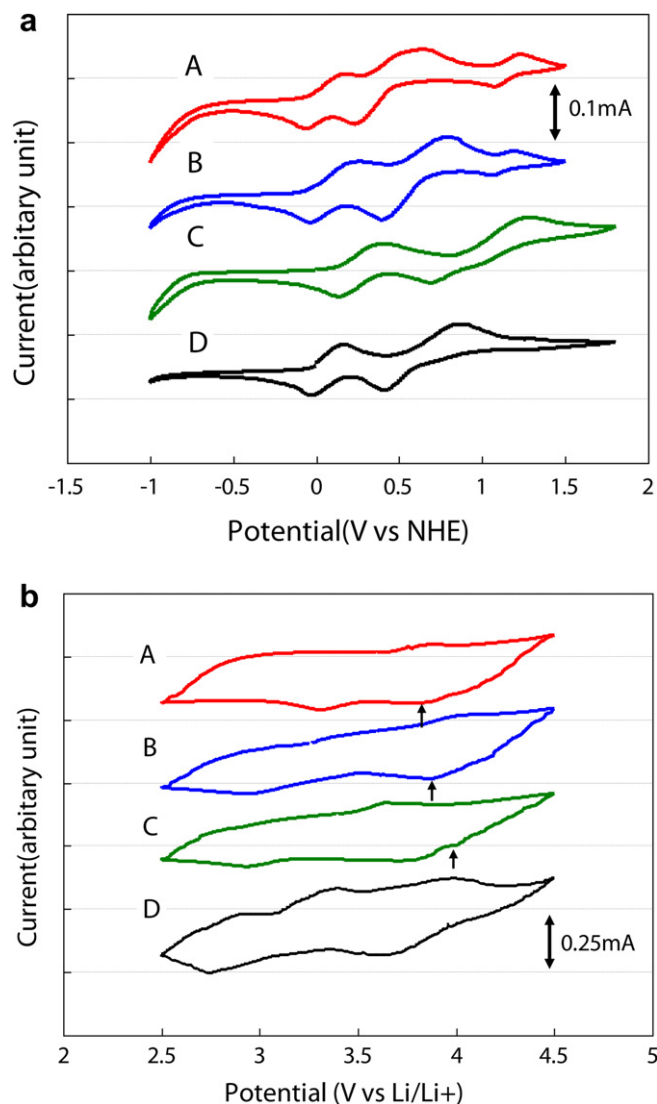


Fig. 1. CV profiles of various iodine solutions using (a) Pt and (b) Li as a reference electrode. The solvents used were dimethyl sulfoxide (DMSO, profile A), tetramethylene sulfoxide (TMSO, profile B), trimethyl phosphate (TMP, profile C), and propylene carbonate (PC, profile D). The concentration of iodine was 0.005 mol L^{−1}. The scan rate was 10 mV s^{−1}.

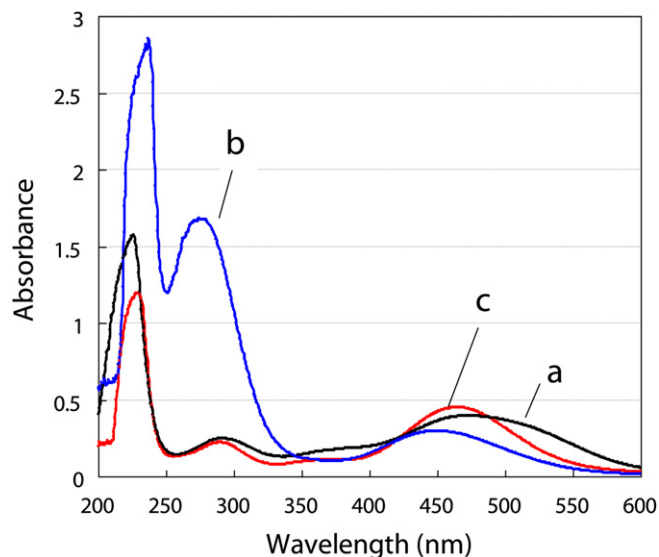


Fig. 2. UV-vis absorption spectra of iodine solutions: (a) PC, (b) TMSO, and (c) TMP.

at -0.02 V, as well as a new reduction signal at $+1.06$ V with a corresponding oxidation at $+1.25$ V. The reduction and oxidation at a high potential (above $+1.0$ V) also appeared in the iodine-DMSO solution (profile A). The TMP solution exhibited two reduction peaks at $+0.11$ V and $+0.66$ V, and a shoulder reduction signal at about $+0.95$ V (profile C, arrow). The scan range was between -1.0 V and $+1.8$ V. When the profiles of the iodine-TMP and iodine-PC solutions were compared, it was observed that the CV profile of the TMP solution shifted to a higher potential.

Fig. 1b shows CV curves of dilute iodine solutions using a lithium foil metal reference electrode. Although the CV curves were broad, reduction signals at high potentials were appeared in iodine solutions except for iodine-PC solution. The DMSO and TMSO showed the reduction peak at 3.83 V and 3.87 V vs. Li/Li^+ , respectively. A shoulder was observed at 3.93 V in the curve of the TMP solution.

3.2. UV-vis absorption spectra of iodine solutions

UV-vis absorption spectra of iodine solutions in PC, TMSO and TMP were measured in order to investigate the electronic

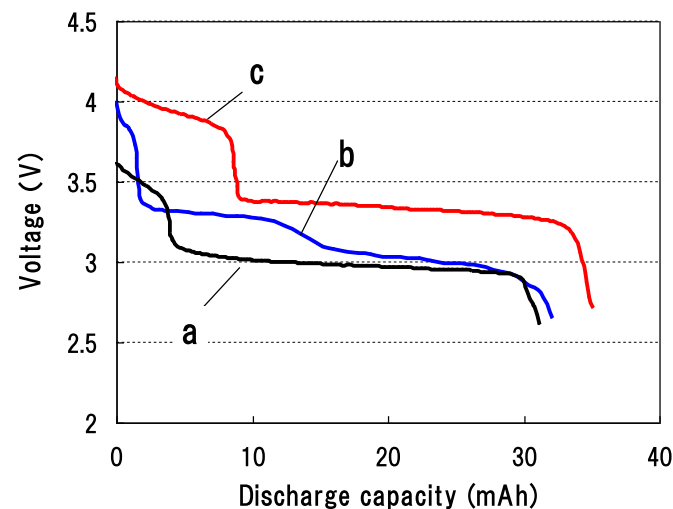


Fig. 3. Discharge curves of electrochemical cells using iodine solutions in various solvents: (a) PC, (b) TMSO, and (c) TMP. The concentration of iodine was 0.075 mol L^{-1} .

properties of the 1:1 complex of I_2 and solvent. In the I_2 -PC solution (spectrum A in Fig. 2), four absorption peaks due to the iodine species were detected at 471 nm, 365 nm, 290 nm, and 227 nm. The signals at 471 nm and 227 nm were assigned to iodine vibrations, analogous to iodine-heptane solutions, which show vibration signals at 520 nm and 229 nm [15]. Thus, iodine molecules in the PC solution formed molecular complexes with PC molecules, with the 520 nm absorption blue-shifted to 471 nm. The signals at 365 nm and 290 nm in Fig. 2 may be attributable to the vibrations of triiodide [16].

The TMSO solution exhibited different UV-vis behavior (spectrum B), with absorption peaks at 450 nm and 274 nm. The former signal for the vibration of iodine was blue-shifted from 520 nm. Meanwhile, the absorption bands at 290 nm and 365 nm for I_3^- were weak, particularly the peak at 365 nm. It was remarkable that the absorption band at 274 nm, which did not seem to arise from I_3^- , was enhanced. De Maine has assigned the peak at 290 nm to I_4 species [17]. Therefore, the absorption band at 274 nm may be due to the 1:1 complex rather than to triiodide. It also suggests

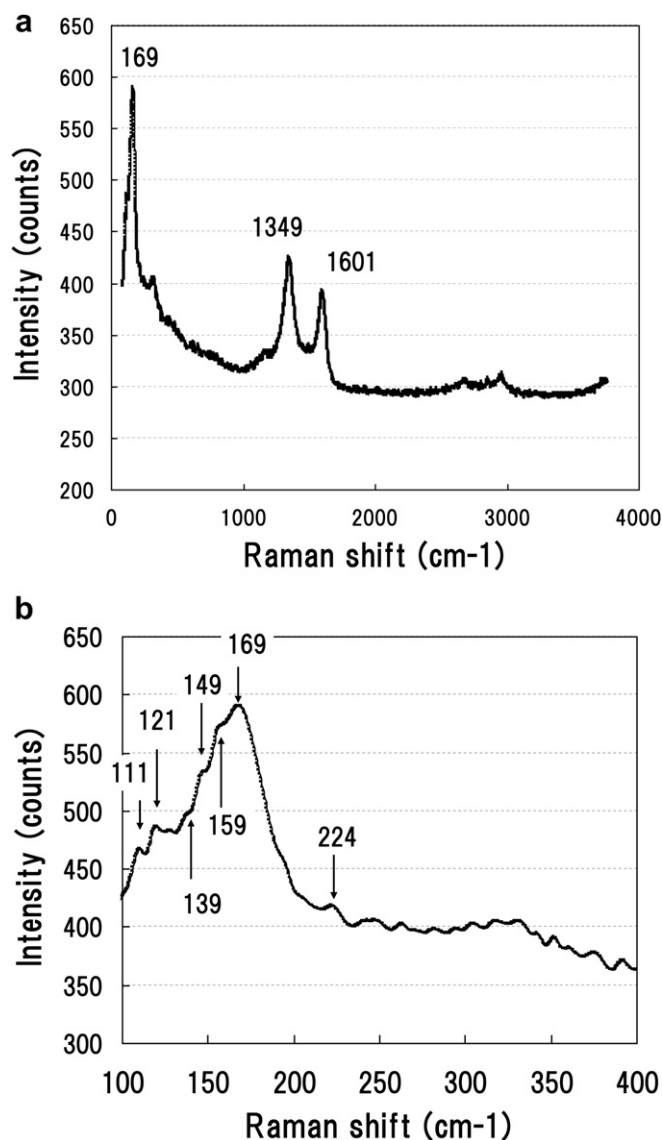


Fig. 4. Raman spectra of the precipitates at the cathode of the TMP cell after discharging of 2 mAh in the wide range of 100 cm^{-1} to 3750 cm^{-1} (a), and in the short range of 100 cm^{-1} to 400 cm^{-1} (b).

the possible formation of a dimer of the 1:1 complex, [TMSO:I₂:TMSO].

In the TMP solution, the absorption usually found near 500 nm appeared at 462 nm instead (spectrum C). As with the PC solution, which had an absorption at 471 nm, this band was slightly blue-shifted in the TMP solution. The absorption bands at 290 nm and 365 nm for I₃⁻ were not shifted.

The variability in these UV–vis absorptions may be attributed to differences in the degree of charge transfer interaction between iodine and the solvent. The band-gap energy E_g for the 1:1 complex of iodine and the solvent has been calculated from the absorption data using the Mie equation, $\lambda = 1240/E_g$ [18]. The values of E_g for iodine complexes with TMSO and with PC were 2.756 eV (450 nm) and 2.633 eV (471 nm), respectively, reflecting a possible shift in the iodine LUMO level. As for the 290 nm band, the blue-shift of this absorption peak to 274 nm reflected an increase in band-gap energy by 0.251 eV (= 4.526 eV–4.275 eV). The band-gap energy for iodine complexes with TMP was 2.684 eV (462 nm).

From Figs. 1a and 2, it was deduced that the unusual reduction near +1.0 V vs. NHE for iodine dissolved in TMSO and TMP was likely to be caused by a shift in the LUMO level of iodine species.

3.3. Discharging behavior

According to our CV studies, a new reduction process occurred in the TMSO, DMSO, and TMP solutions of iodine, indicating that Li–I₂ batteries using those solvents discharged near +4.0 V vs. Li⁺/Li. Li–I₂ electrochemical cells using PC, TMSO, and TMP were fabricated and tested to elucidate their discharging behavior. Fig. 3 shows discharge curves of the Li–I₂ electrochemical cells at 25 °C. The discharge current was 0.05 mA cm⁻²-cathode area. As shown in Fig. 1a, the iodine-TMSO solution had three reduction peaks, indicating that Li–I₂ electrochemical cells using TMSO would discharge in three stages. In the cell using this solvent, three stages for discharging were actually observed. The cell exhibited an open-circuit voltage (OCV) of 3.99 V and discharged near 4.0 V (curve B). The discharge capacity at the first stage (about 4.0 V) was about 2 mAh.

This was 6.2% of the total discharge capacity of 32.1 mAh. The cell with DMSO showed the same discharging behavior as the TMSO cell. The OCV of the DMSO cell was also 3.93 V, but in this cell, the first stage (near 4.0 V) was brief, with a drop in voltage within the initial discharging stage. In Li–I₂ batteries, lithium iodide is mainly formed on the carbon cathode during discharging, and is dissolved in the DMSO. The dissolved LiI may be associated with iodine molecules, and then converted Li⁺ and I₃⁻ ions in the electrolyte. As the cell containing I₃⁻ operates at about 3.3 V, it was surmised that the voltage drop on discharge was caused by dissolution of lithium iodide from the cathode.

Concerning the I₂-PC cell, two discharge stages were observed, at about 3.5 V and 3.0 V, respectively. These results correlated well with the CV profile of the I₂-PC solution. The OCV of the PC cell was 3.61 V (curve B).

The Li–I₂ electrochemical cell fabricated with TMP had an OCV of 4.14 V and a discharge potential of more than 4.0 V (curve C). The anomalous discharging behavior above 4.0 V was caused by the reduction shoulder at +0.95 V in Fig. 1a. This cell showed a two-stage discharge. The discharge capacity at the first stage (about 4.0 V) was about 8.6 mAh. This was 24.5% of the total discharge capacity of 35.1 mAh.

3.4. Analysis

The Li–I₂ electrochemical cells fabricated with TMSO and TMP discharged near 4.0 V. In order to examine the electrochemical reaction near 4.0 V, the precipitates formed at the cathodes in these cells after discharging at 2 mAh were analyzed by Raman and SIMS techniques. Raman signals for the precipitates at the cathode in the TMP cell are displayed in Fig. 4a and b. The signal at 169 cm⁻¹ is due to vibration of iodine compound. The two strong peaks at 1349 cm⁻¹ and 1601 cm⁻¹ reflect D and G bands of Ketjen black in the cathode, respectively. Fig. 4b shows a Raman spectrum in the range of 100 cm⁻¹ and 400 cm⁻¹. The signal at 111 cm⁻¹ and the shoulder at 139 cm⁻¹ are ascribed to vibration of I₃⁻. From the peaks at 121 cm⁻¹, 149 cm⁻¹, 159 cm⁻¹ and 169 cm⁻¹, it was found that

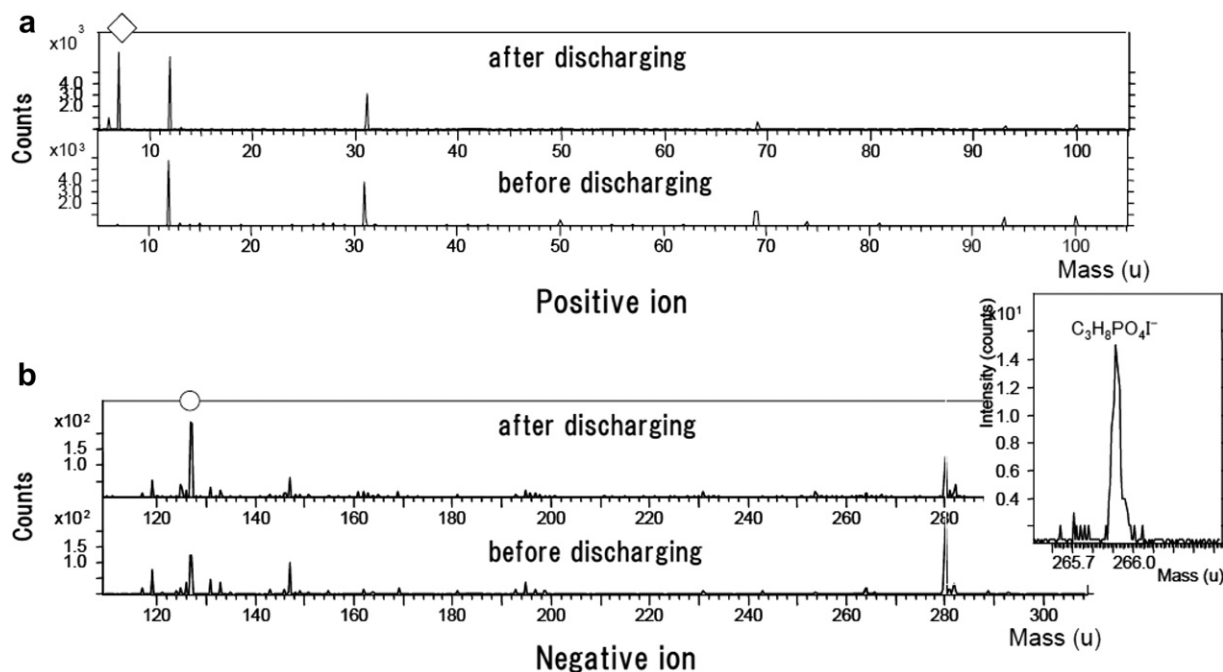
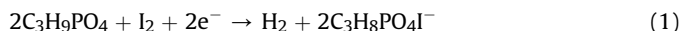


Fig. 5. SIMS spectra of the cathodes of the TMP cell before and after discharging: (a) positive-ion mode and (b) negative ion mode. The discharge capacity was 2 mAh. The signal intensities at $m/z = 7$ (\diamond) and $m/z = 127$ (\circ) correspond to the amounts of Li⁺ and I⁻, respectively. The inset shows a SIMS signal at $m/z = 265.9$, assigned to C₃H₈PO₄I⁻.

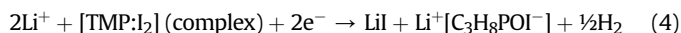
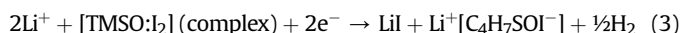
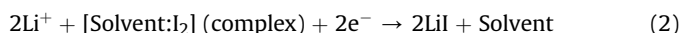
bent-type I_5^- existed at the cathode [19,20]. These polyiodides were formed by an association of lithium iodide and I_2 .

The main precipitate during discharging in the Li– I_2 electrochemical cell is lithium iodide. However, Raman technique is inactive to vibration of LiI. We have used SIMS spectrometry to elucidate LiI at the cathode. The area of the SIMS measurement was $0.5\text{ mm} \times 0.5\text{ mm}$. Fig. 5 shows positive-ion and negative-ion SIMS spectra for the TMP cell before and after discharging. The intensities of the signals at $m/z = 7$ (\diamond , Li^+) and $m/z = 127$ (\circ , I^-) were enhanced after discharging, indicating that lithium iodide was mainly formed at the cathode during discharging. A big signal around at $m/z = 280$ was ascribed to TFSI anion. The intensity due to I_3^- at $m/z = 381$ was very weak. The signal of I_5^- at $m/z = 635$ was not detected. Comparable SIMS data were measured for the TMSO cell.

A negative ion signal at $m/z = 265.9$ was seen in the SIMS spectrum from the cathode for the discharged TMP cell (inset in Fig. 5), with an intensity of order 10. It is proposed that this signal arose from $C_3H_8POI^-$ formed by the elimination of a proton from TMP, $C_3H_9PO_4$ (Eq. (1)):



In the SIMS analysis of the TMSO cell, a negative ion signal at $m/z = 229.9$ was detected, corresponding to $C_4H_7SOI^-$. These results suggested that TMP and TMSO molecules decomposed slightly during the discharging. It was concluded that Eq. (2) was the main electrochemical reaction near +4.0 V, with the possible occurrence of the side reactions given by Eqs. (3) and (4) during discharging:



In Eqs. (3) and (4), hydrogen generates during discharge process. The GC/MS measurement of gasses in the electrochemical cells after discharging of 8 mAh was made. We detected hydrogen, carbon monoxide, and carbon dioxides in the TMP cell. The amount of hydrogen was 0.064 cc, corresponding to 0.18% of all gasses. The rate of gas generation was 0.008 cc per discharge capacity

(cc/mAh). The rates of CO and CO_2 were 0.001 cc/mAh and 0.003 cc/mAh, respectively. However, the PC cell also included hydrogen of 0.005 cc/mAh. The results suggest a possibility that the hydrogen generation in the TMP cell was caused not only by the side reaction of Eq. (4) but by other reaction such as solvent decomposition at lithium negative electrode.

4. Conclusions

It is generally accepted that Li– I_2 electrochemical cells undergo discharge below 3.5 V. In this study it was found that the iodine molecules complexed with sulfoxides or trimethyl phosphate reacted with Li ions at high potentials, near 4.0 V. We have demonstrated that Li– I_2 batteries using TMSO or TMP operate at about 4.0 V. The electrochemistry involved a molecular complex of iodine with the solvent. This basic mechanism of the interaction between the molecular complex and Li ion could be exploited to design other halogen batteries.

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